Trajectory hunting: Analysis of UARS measurements showing rapid chlorine activation

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Abstract. Trajectory hunting (i.e., a technique to find air parcels sampled at least twice over the course of a few days) is applied to analyze Upper Atmosphere Research Satellite (UARS) measurements in conjunction with the AER photochemical box model. In this study, we investigate rapid chlorine activation in the Arctic lower stratosphere on 29 Dec 1992 associated with a polar stratospheric cloud (PSC) event. Six air parcels that have been sampled twice were followed along 5-day trajectories at the 465 K ($\sim$46 mb) and 585 K ($\sim$22 mb) levels. A detailed sensitivity study with the AER photochemical box model along these trajectories leads to the following conclusions for the episode considered: (1) model results are in better agreement with UARS measurements at these levels if the UKMO temperature is decreased by at least 1-2 K; (2) the NAT (nitric acid trihydrate) PSC formation scheme produces results in better agreement with observations than the STS (supercooled ternary solution) scheme; (3) the model can explain the UARS measurements at 585 K, but underestimates the ClO abundance at 465 K, suggesting some inconsistency between the UARS measurements at this level.

Introduction

To understand the current and predict the future ozone depletion in the polar regions it is necessary to separate the effects due to dynamical and chemical processes. One effective strategy for achieving this goal is to identify air parcels that have been sampled twice over the course of a few days. The difference between initial and final concentrations of ozone (or any other species) for these parcels can be attributed solely to chemical processing since dynamical effects are eliminated. This Lagrangian approach has been used by *von der Gathen et al.* [1995] and *Rex et al.* [1998] to quantify chemical ozone depletion from ozonesondes launched at different points along a parcel trajectory ("matches") in the Arctic. *Becker et al.* [1998] used a photochemical box model to analyze the measured O_3 loss along matched parcels. This technique can also be applied to measurements obtained by different platforms. For example, *Pierce et al.* [1997] compared trajectory-matched observations from the UARS Halogen Occultation Experiment (HALOE) with aircraft ER-2 measurements. *Bacmeister et al.* [1998] applied trajectory mapping to a comparison of long-lived tracer data obtained by the ER-2 and CRyogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) in November 1994.

Analysis of short-lived species along parcel trajectories requires a photochemical model. Utilization of UARS

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Cryogenic Limb Array Etalon Spectrometer (CLAES) and Microwave Limb Sounder (MLS) data combined with a photochemical box model looks particularly promising in this context due to a relatively large number of measured species (O_3, HNO_3, ClO, $ClONO_2$, N_2O, CH_4, H_2O) and very frequent sampling ($\sim$1300 profiles per day). The goal of this study is to compare the AER box model representation of photochemical and PSC processes with the UARS measurements for air parcels sampled twice and to check the consistency between CLAES and MLS data.

Identification of matched trajectory

We examine an episode of rapid chlorine activation associated with PSC activity in the Arctic polar region. We concentrated on events for which the evidence of chlorine activation is unambiguous, i.e., daytime MLS measurements showing unenhanced values of ClO immediately prior to formation of a PSC. In one such episode, the ClO concentration increased from near zero on 24 Dec 1992 to 1.4 (0.8) ppbv on 29 Dec 1992 at 465 K (585 K) (see Figure 1). For this case, 400 equally spaced parcels were initialized in a $20° \times 40°$ latitude/longitude box encompassing the enhanced ClO points on 29 Dec and 5-day isentropic back trajectories were calculated using the model described by *Manney et al.* [1994] (with horizontal winds and temperatures from the UKMO data assimilation). Because diabatic effects are negligible over a 5-day interval in the lower stratosphere, cross-isentropic flow was ignored. From this original set of parcels, we identified candidate parcels that were nearly coincident (in space and time) with enhanced ClO points on 29 Dec and with any MLS measurement points 5 days earlier on Dec 24. Also, both initial and final points of these parcels were within the vortex (based on UKMO potential vorticity gradients). The number of matches depends on the number of individual enhanced ClO points, the number of parcels initialized in the original box, the meteorological conditions, and of course the "match" criteria. For example, sensitivity studies show that for the episode considered, the number of matches drops from 52 (35) at 465 K (585 K) for $\Delta t \leq 2$ h, Δlatitude $\leq 4°$, Δlongitude ≤ 350 km to 14 (6) for $\Delta t \leq 2$ h, Δlatitude $\leq 2°$, Δlongitude ≤ 200 km. Many matches are duplicative in the sense that several parcels may start off near the same high-ClO point, follow similar paths, and thus also end up nearest the same point at the termination of the back trajectory calculation. For the results discussed below, we have selected a subset of 6 parcels on each level that represents the widest range of behavior possible; all selected parcels satisfy the stricter match criteria ($\Delta t \leq 2$ h, Δlatitude $\leq 2°$, Δlongitude ≤ 200 km). Other uncertainties associated with the match technique are discussed in *Rex et al.* [1998]. Note that this technique should only be used for simulations shorter than $\sim$10 days because of the large uncertainties in trajectory calculations done for longer periods.

Model Initialization

The AER photochemical box model [*Danilin et al.*, 1998] with NAT and STS PSC schemes and the recommended list of heterogeneous reactions [*DeMore et al.*, 1997] is used. The NAT surface area density (SAD) is calculated assuming a particle diameter of 1 μm with a density of 1.62 g/cm^3, while the STS SAD is defined according to [*Tabazadeh et al.*, 1994] keeping the particle concentration constant. The values of the MLS and CLAES species are obtained at the exact initial and final parcel positions through interpolation. The model is initialized using MLS version 4 (v.4) O_3 (profiles and column above 100 hPa) and HNO_3, prototype non-linear retrievals of MLS H_2O [*Pumphrey*, 1998], and CLAES version 8 (v.8) $ClONO_2$, N_2O, and CH_4. Total inorganic chlorine, Cl_y, is defined from the Cl_y-N_2O correlation according to *Woodbridge et al.* [1995] using CLAES measurements of N_2O at the initial points; this approach produces 2.0-2.5 ppbv and ~2.9 ppbv of Cl_y at 465 K and 585 K, respectively. For all trajectories, ClO is initialized to ClO^{MLS}. Since no HALOE HCl measurements are available for the points of interest, initial HCl is set to $Cl_y - ClONO_2^{CLAES} - ClO^{MLS}$. Total inorganic bromine, Br_y, is defined according to *Wamsley et al.* [1998] with initial $BrO=BrONO_2=Br_y/2$. Since no reliable NO_x ($= NO+NO_2$) measurements are available for the points considered, we perform a sensitivity study in which NO_x is set to 2 pptv or 0.2 ppbv (based on aircraft measurements [*Kawa et al.*, 1992]), and we assume that initial $NO=NO_2=NO_x/2$. Total reactive nitrogen, NO_y, is taken to be $HNO_3^{MLS} + ClONO_2^{CLAES} + NO_x$. Sulfate aerosol surface area is initialized according to *Massie et al.* [1998] using the CLAES aerosol extinction measurements at 780 cm^{-1}.

Results of trajectory calculations

MLS detected a rapid increase in ClO of 0.5-1 ppbv in the lower stratosphere above northern Canada between 24 Dec and 29 Dec 1992 (Figure 1). Six air parcels that satisfy the match criteria described above are also shown in Figure 1, together with the temperature and solar zenith angle (SZA) along their trajectories. Temperatures dipped below 195 K in the 1-2 days preceding the MLS observation of high ClO, suggesting that PSC processing converted chlorine into Cl_2 and Cl_2O_2, which were photolyzed to ClO at the final points (where SZA≤90°).

Figure 2 compares model results and data for ClO and $ClONO_2$ along the trajectory of parcel #A at 585 K and parcel #a at 465 K. The blue curves depict the behavior for the NAT PSC scheme and UKMO temperature. It is obvious that this approach cannot explain the ClO measurements. *Manney et al.* [1996] showed that, compared to radiosondes, UKMO temperatures have a systematic warm bias of ~1-3 K during most of the northern winter. To explore the possible influence of such a temperature bias, we show model results for the NAT scheme with the UKMO temperature lowered

by 2 K. In this case (grey lines), the model agrees with the ClO measurements at 585 K, but overestimates the $ClONO_2$ depletion. By additionally increasing the initial $ClONO_2$ by 15% [*Mergenthaler et al.*, 1996] (while keeping Cl_y constant), the model (green lines) can be made to agree with the measurements at 585 K. However, the model still underestimates ClO and $ClONO_2$ at 465 K even with all these adjustments. For the STS scheme (red lines), the model underestimates ClO at both levels. The CLAES v.8 aerosol extinction measurements (converted to SAD) are consistent with the model calculations in the final points. However, these measurements are not useful for distinguishing between the NAT ans STS schemes during the episode considered since the PSC event was not captured in the final points of the matched trajectories. Very similar results are obtained for the other parcels and are not shown here. Comparisons of model results and UARS measurements are not shown for O_3 and HNO_3 since the differences between their initial and final values are small and generally consistent with the model within the range of the measurement uncertainties.

Table 1 summarizes our model sensitivity analysis for all parcels. The model can be made to agree with the ClO and $ClONO_2$ measurements along each parcel trajectory at 585 K by varying the temperature or the initial $ClONO_2$ or NO_x within reasonable ranges. However, there is a persistent model underestimate of ClO at 465 K for all considered sensitivity runs. Previous model attempts also underestimated the MLS ClO measurements at 465 K [*Chipperfield et al.*, 1996; *Lutman et al.*, 1997].

Discussion

The failure of the straightforward and well-constrained comparison in our case raises the question of whether the MLS v.4 ClO and CLAES v.8 $ClONO_2$ measurements are consistent at 465 K during/after PSC events.

To answer this question, we estimate the maximum ClO concentrations allowed by stoichiometry arguments based on the following assumptions: (1) the $ClONO_2$ + HCl $\rightarrow$ Cl_2 + HNO_3 reaction is a principal mechanism of chlorine activation, (2) initial [HCl] > initial [$ClONO_2$], (3) initial [Cl_2] and [Cl_2O_2] are very small, and (4) all active chlorine is in ClO at the final point. The first assumption is very reasonable, bearing in mind the temperature history along the trajectories and the temperature dependence of the $ClONO_2$ + H_2O and HOCl + HCl reactions [*DeMore et al.*, 1997]. The second assumption is consistent with N_2OCLAES-derived Cl_y for the episode studied. The third assumption is supported by the warm temperature along the backward trajectories and the ClO and $ClONO_2$ measurements 10 days prior to 24 Dec 1992. suggesting that conversion of HCl and $ClONO_2$ to other active chlorine forms (Cl_2O_2 and Cl_2), undetectable by MLS, is unlikely. The fourth assumption is too strong for the final points with SZA of 85°-90°, but it provides an upper bound for ClO. Based on these assumptions, the max-

imum increase in chlorine monoxide, ΔClO^{max}, equals $2 \times ClONO_2{}^{initial} - ClONO_2^{final}$ (since the $ClONO_2 +$ HCl reaction produces Cl_2 until a complete consumption of the smaller reactant (i.e. $ClONO_2{}^{initial}$), and since a part of activated chlorine is converted back to $ClONO_2^{final}$). Taking into account the 15% precision of the CLAES $ClONO_2$ measurements, one gets $\Delta ClO^{MAX} = 2.3 \times ClONO_2^{initial} - 0.85 \times ClONO_2^{final}$. A possibility that the whole initial HCl amount could be consumed requires both prolonged PSC processing in a presence of sunlight and high NO_x (several ppbv). However, this possibility can be ruled out based on the SZA history along these parcels (see Figure 1) and relatively low NO_x (up to 0.2 ppbv) [*Kawa et al.*, 1992].

Table 2 compares the changes in ClO according to the MLS measurements and our stoichiometric calculations. The MLS v.4 ClO and CLAES v.8 $ClONO_2$ data are consistent within the range of their uncertainties if $\Delta ClO^{MLS}\text{-}2\sigma \leq \Delta ClO^{MAX}$. Table 2 shows that these measurements are inconsistent for parcel #b. It is unlikely that these measurements are consistent for parcel #e (where about half of the active chlorine is in the Cl_2O_2 form at the final point, for which SZA≈89°). Analysis of a larger subset of UARS data is required to elucidate whether MLS v.4 overestimates ClO or CLAES v.8 overestimates $ClONO_2$ after PSC events, or whether the model fails to adequately simulate other physical processes. Various refinements to the MLS and CLAES retrieval algorithms are ongoing and future versions of these data sets may exhibit improved consistency with model calculations.

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Figure 1. MLS v.4 ClO (ppbv) at 465 K (left) and 585 K (right) on 29 Dec (top row) and 24 Dec 1992 (second row). Isentropic 5-day back trajectories for 6 air parcels that were sampled twice are overlaid on the 24 Dec plots in the second row, with thick dots corresponding to the locations of the MLS measurements above Canada on 29 Dec that indicate enhanced ClO (defined as >1.0 ppbv at 465 K and >0.75 ppbv at 585 K). The evolution of temperature (third row) and SZA (bottom row) along these trajectories are shown using the same colors as for the parcels.

Figure 2. Comparison of MLS v.4 ClO and CLAES v.8 $ClONO_2$ and aerosol (converted from the 780 cm^{-1} extinction to surface area density, SAD) (black symbols) with AER model calculations along the trajectory of parcels #A and #a (denoted by red lines in Figure 1) at 585 K (top) and 465 K (bottom), respectively. Blue lines: NAT scheme, UKMO temperature; grey lines: NAT scheme, UKMO temperature lowered by 2 K; green and red lines: UKMO temperature lowered by 2 K, initial $ClONO_2$ set to $1.15 \times ClONO_2^{CLAES}$, NAT and STS schemes, respectively. The grey and green lines coincide in the SAD plot.

Table 1. Comparison of model calculations of ClO and ClONO$_2$ at the final points with UARS measurements. "T" and "T-2K" denote the NAT scheme with T^{UKMO} and $T^{UKMO} - 2$ K, respectively; "STS" denotes the STS scheme with $T^{UKMO} - 2$ K; "fit" denotes the NAT scheme with $T^{UKMO} - 2$ K and initial ClONO$_2$ and NO$_x$ varying from ClONO$_2^{CLAES}$ to $1.15 \times$ClONO$_2^{CLAES}$ and from 0.002 to 0.2 ppbv, respectively.

Species	Par-cel	465 K UARS, ppbv	T, NAT	Model T-2K, NAT	T-2K, STS	Par-cel	585 K UARS, ppbv	T, NAT	Model T-2K, NAT	T-2K, STS	fit, NAT
ClO	a	1.10±0.48	0.07	0.44	0.18	A	0.79±0.38	0.24	0.78	0.24	0.41
ClONO$_2$		0.64±0.10	0.59	0.36	0.51		0.94±0.14	0.88	0.68	0.88	0.88
ClO	b	1.28±0.49	0.39	0.58	0.42	B	0.82±0.38	0.20	0.24	0.20	0.43
ClONO$_2$		0.33±0.05	0.30	0.04	0.15		0.87±0.13	0.90	0.91	0.92	0.86
ClO	c	1.39±0.49	1.02	1.05	1.02	C	0.88±0.39	0.21	0.26	0.21	0.51
ClONO$_2$		0.50±0.08	0.07	0.01	0.05		0.95±0.14	0.94	0.95	0.95	0.87
ClO	d	1.39±0.49	0.86	0.97	0.72	D	0.81±0.38	0.26	1.26	0.23	0.51
ClONO$_2$		0.65±0.10	0.17	0.02	0.28		1.21±0.18	0.86	0.40	0.88	1.17
ClO	e	1.49±0.49	0.71	0.71	0.71	E	0.78±0.38	0.19	0.55	0.20	0.57
ClONO$_2$		0.37±0.06	0.02	0.01	0.00		1.18±0.18	0.95	0.81	0.95	1.00
ClO	f	1.49±0.49	0.79	0.82	0.76	F	0.78±0.38	0.09	0.28	0.09	0.41
ClONO$_2$		0.40±0.06	0.07	0.01	0.01		1.10±0.17	0.96	0.90	0.96	0.97

Table 2. Change in ClO (ppbv) between final and initial points at 465 K according to MLS v.4 data and stoichiometric calculations (see text).

parcel	MLS		Stoichiometry	
	ΔClO	ΔClO-2σ	ΔClO^{max}	ΔClO^{MAX}
a	1.11	0.54	0.58	0.86
b	1.28	0.71	0.47	0.64
c	0.82	0.25	0.68	0.94
d	0.82	0.25	0.49	0.76
e	0.92	0.35	0.39	0.56
f	0.92	0.35	0.72	0.94

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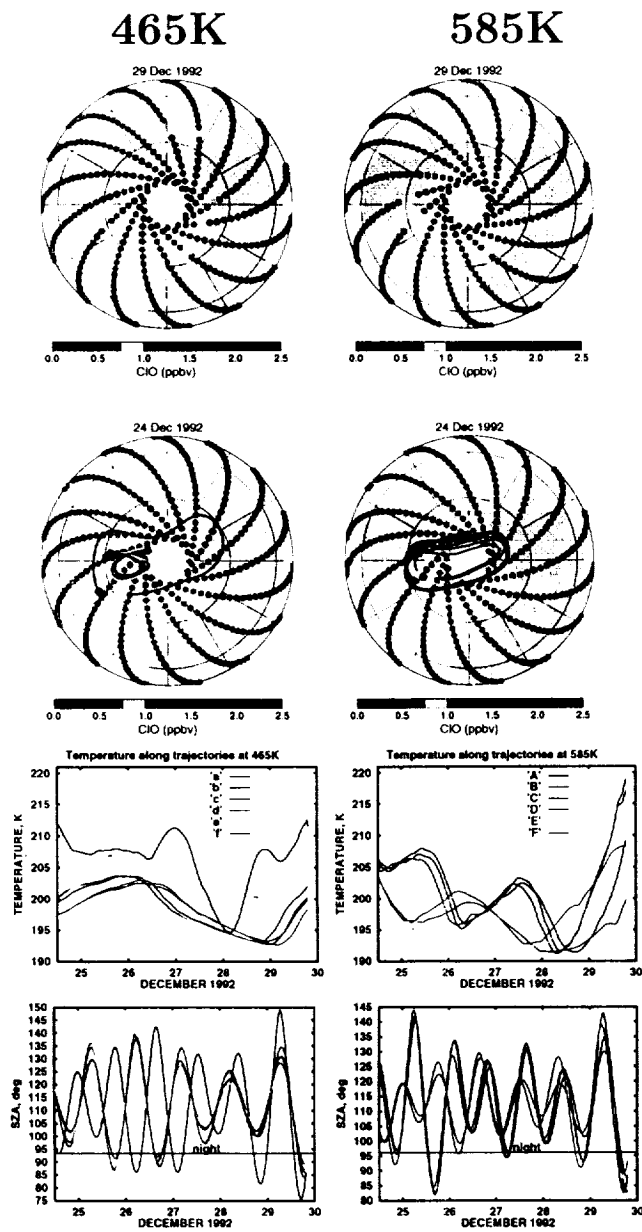DANILIN ET AL.: TRAJECTORY HUNTING: ANALYSIS OF UARS DATA

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Figure 1. MLS v.4 ClO measurements (in ppbv) at 465 K (left column) and 585 K (right column) on Dec 29 (top row) and Dec 24, 1992 (second row). Six air parcels sampled twice are shown in the second row with thick dots (final points) corresponding to the locations of MLS measurements on Dec 29, 1992 showing high ClO content above Canada (red dots at 465 K and yellow dots at 585 K). Evolutions of temperature (third row) and SZA (low row) along these parcels are also shown by the same colors as the parcels.
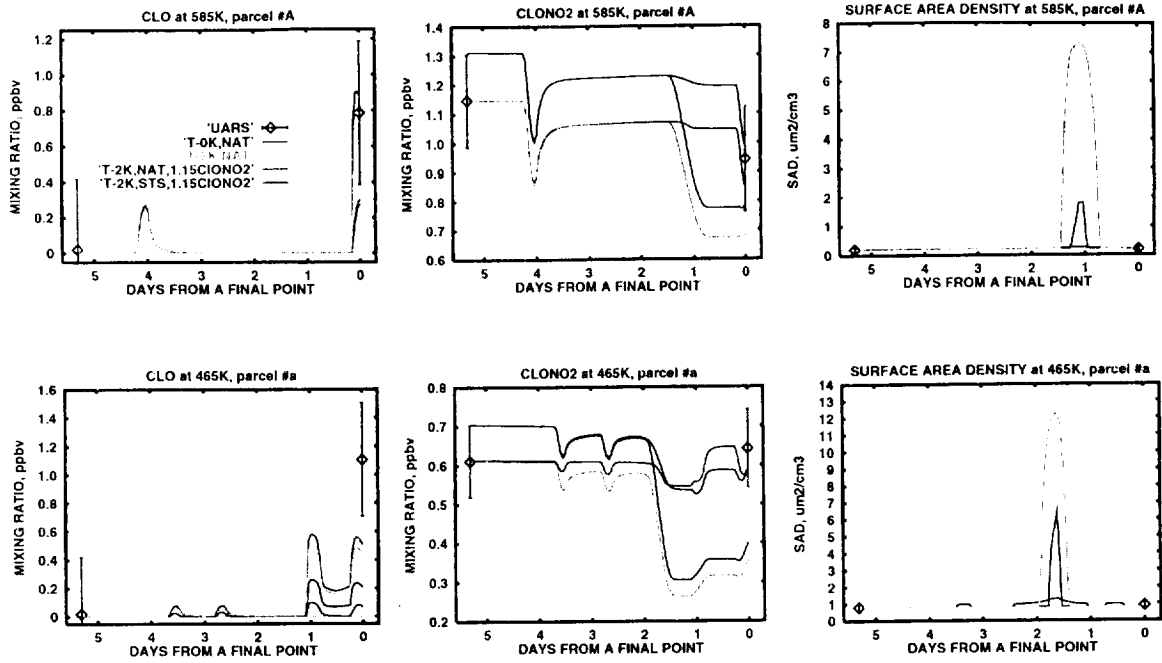
Figure 2. Comparison of MLS v.4 ClO and CLAES v.8 $ClONO_2$ and aerosol (converted from the 780 cm^{-1} extinction to SAD) measurements (black symbols) at 465 K (bootom line) and 585 K (top line) with AER model calculations for the parcels #a and #A (i.e. shown by red lines in Figure 1). Blue lines: NAT scheme, UKMO temperature; grey lines: NAT scheme, UKMO temperature lowered by 2 K; green and red lines: UKMO temperature lowered by 2 K, initial $ClONO_2$ equals to $1.15ClONO_2^{claes}$, NAT and STS schemes, respectively. The grey and green lines coincide at the SAD plot.